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Investigation of the effect of treatment with supercritical carbon dioxide on structure and properties of polypropylene microfiltration membranes

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ABSTRACT

The effects of treatment with supercritical carbon dioxide of two types of polypropylene microfiltration membranes, which may occur in novel membrane processing techniques such as membrane cleaning using supercritical carbon dioxide as solvent, were investigated. The membranes were treated with $scCO_2$ at three different pressures (8 MPa, 16 MPa, and 24 MPa) and at two various temperatures (40 °C and 70 °C) for different treatment times (5 min and 100 min). The morphology of the membranes was investigated using various analytical methods, using non-treated membranes as reference samples. No critical changes in membrane structure and properties, which would limit the usability of the membranes in microfiltration processes, were observed. Supercritical carbon dioxide can be safely applied in polypropylene membrane production, maintenance and modification.

1. Introduction

Porous polymer membranes are widely used in such fields as chemical industry, biotechnology and medicine. In numerous membrane production, maintenance and modification technologies, large amounts of organic solvents are used, which generates problems in terms of process safety, environmental hazard and the cost-effectiveness of the technologies. For example, during production of microfiltration membrane using the Temperature Induced Phase Separation (TIPS) method [1,2], the raw membrane contains oils resulting from the phase separation, which fill its porous body and which have to be removed before normal usage. In the traditional cleaning method, hot isopropyl alcohol is used for this purpose as solvent; however, this approach is characterized by high cost, potential environmental load and fire hazard due to high flammability of the organic solvent.

As in many other technologies, drawbacks related to the use of organic solvents can be reduced or even eliminated by replacing them with supercritical fluids (SCFs) [3]. Supercritical carbon dioxide ($scCO_2$) is the most commonly used SCF and exhibits numerous advantages such as moderate critical parameters, non-flammability, non-toxicity, good availability. The use of $scCO_2$ as reaction or separation medium instead of organic solvents enables to adapt established technologies to the principles of green chemistry and green engineering [4]. There are already examples of efficient membrane cleaning [5], production [6–8], and chemical modification [9]. technologies employing supercritical carbon dioxide. Supercritical carbon dioxide can be regarded as promising "green" medium for development of novel membrane processing technologies.

However, it is known that treatment with supercritical carbon dioxide ($scCO_2$) may cause significant changes in the internal structure of polymers [10]. This also applies to polypropylene [11–13], which is a common raw material for production of microfiltration membranes. Moreover, changes in structure and properties of reverse osmosis membranes after treatment with scCO2 were reported as well [14]. Such structural changes do not disqualify the use of $scCO_2$ provided that they do not affect significantly the basic mechanical properties of the membranes, which define their usability in membrane separation processes, such as mechanical strength, pore diameter distribution, etc. Preliminary tests did not identify any critical structural changes in polypropylene microfiltration membranes exposed to $scCO_2$ [15]. However, a broad range of process parameters, which may occur in novel technologies for membrane processing, should be investigated to confirm that $scCO_2$ is a safe medium for these applications.

The aim of this study was to investigate the impact of $scCO_2$ treatment in various process conditions–including typical conditions for membrane cleaning processes [5] – on structure and properties of porous polypropylene membranes used in microfiltration and to assess whether $scCO_2$ can be used as a safe

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medium for membrane cleaning, maintenance and modification technologies without destroying the membrane's key features.

2. Methods

As test material, commercially available polypropylene microfiltration membranes from two manufacturers (Membrane A–PolyMemTech Sp. z o.o., Poland, and Membrane B: Membrana GmbH, Germany) were used. The membranes have a hollow-fiber geometry with similar dimensions (Membrane A: outer diameter 2.8 mm, inner diameter 1.9, surface porosity ca. 47%; Membrane B: outer diameter 2.7 mm, inner diameter 1.8, surface porosity ca. 70%).

In the first part of experimental investigation, treatment of the membrane with supercritical carbon dioxide (99.995%, Linde Gaz sp. z o.o., Poland) in a high pressure experimental system – including a $scCO_2$ pump, a high pressure vessel and a process conditions control unit – was carried out. The following process conditions were varied: pressure (80, 160, and 240 bar), temperature (40, and 70 °C), treatment time (5, and 100 min), and depressurization rate (F–fast, i.e. instantaneous depressurization, and S–slow, with depressurization rate–2 bar/ min, only for experiments with 100 min treatment time). This range of process parameters includes typical conditions for the process of membrane cleaning using $scCO_2$. After the $scCO_2$ treatment, the structure and properties of the membranes were investigated. Membrane samples not treated with CO_2 were employed as reference samples. For assessment of changes of membrane structure and properties, four analytical methods were applied: scanning electron microscope (SEM), tensile test, contact angle measurement, and the bubble point experiment.

A scanning electron microscope Phenom G2 Pro (Phenom-World, The Netherlands) was used for assessment of the morphology of the membranes. Side surface and cross-sections (obtained by fracture after immersion in liquid nitrogen) of membranes were investigated at different magnifications in order to detect possible changes of the structure. In order to estimate the mechanical strength of the membrane samples, tensile tests were conducted using a universal testing machine Instron 5566 (Instron, USA). In each series, six samples (50 mm in length) were stretched until break (elongation rate: 15 mm/min), stress–strain curves were plotted and mean values of selected parameters (Young's modulus, ultimate tensile strength and maximum elongation at break) were determined. The wetting properties of the membranes were investigated by measurement of the contact angle (dynamic Wilhelmy method) using the Krüss Processor Tensiometer K12 (Krüss, Germany). Advancing and receding contact angle values were calculated as average values from ten measurements in each series. The bubble point method was employed in order to evaluate other parameters of the porous membranes, such as the number of pores, pore size distribution, filtration coefficient UFC and surface porosity. Membrane modules were prepared and immersed in an isopropyl alcohol bath. The volume flow rate of air was measured as function of increasing transmembrane pressure. From this relationship, the pore size distribution was reconstructed and the abovementioned parameters were calculated.

3. Results and discussion

In Table 1, a summary of experimental results is presented. For both membrane types, the reference values are shown together

Table. 1
Summary of experimental results.

Parameter	Membrane A			Membrane B		
	Reference	Max. value (conditions)	Min. value (conditions)	Reference	Max. value (conditions)	Min. value (conditions)
Tensile tests						
Young's modulus [MPa]	92,01	103.74 (+13%) (160/70/100/S)	85.39 (−7%) (80/70/5/F)	87.61	95.08 (+9%) (160/40/100/S)	81.78 (−7%) (80/40/5/F)
Ultimate tensile strength [MPa]	3.54	3.84 (+8%) (160/70/100/S)	3.20 (−10%) (240/40/5/F)	3.73	3.79 (+2%) (80/40/100/F)	3.67 (−2%) (240/70/5/F)
Max elong. at break [%]	168.25	177.97 (+6%) (240/70/5/F)	66.88 (−60%) (240/70/100/F)	172.82	183.34 (+6%) (240/70/5/F)	170.29 (−1%) (80/70/5/F)
Contact angle						
Advancing [°]	100.9	114.3 (+13%) (80/40/100/S)	96.1 (−5%) (80/40/100/F)	115.2	117.4 (+2%) (80/70/100/S)	101.1 (−12%) (160/70/5/F)
Receding [°]	51.4	61.7 (+ 20%) (80/40/5/F)	44.7 (−13%) (240/70/100/F)	48.7	49.8 (+2%) (160/70/5/F)	38.5 (−21%) (80/70/100/S)
Bubble point						
Mean pore size [μm]	0.284	0.352 (+24%) (160/70/100/F)	0.249 (−12%) (240/70/100/S)	0.447	0.456 (+2%) (160/40/100/F)	0.425 (−5%) (160/40/5/F)
Pore size SD [μm]	0.068	0.069 (+24%) (160/70/100/F)	0.039 (−43%) (240/70/100/S)	0.071	0.078 (+10%) (80/70/5/F)	0.040 (−44%) (160/40/100/F)
No of pores [10^9/ m^2]	19943.76	65907.12 (+230%) (240/70/100/S)	12705.69 (−36%) (160/70/100/F)	7065.42	22586.79 (+220%) (160/40/100/F)	7001.57 (−1%) (160/70/100/F)
UFC [ml/bar cm^2 min]	0.89	1.10 (+24%) (160/40/100/F)	0.66 (−26%) (240/70/100/F)	1.36	1.98 (+46%) (160/70/5/F)	1.17(−14%) (80/70/5/F)

(Process conditions: (pressure [MPa]/temperature [°C]/time [min]/decompression mode: Slow/Fast)

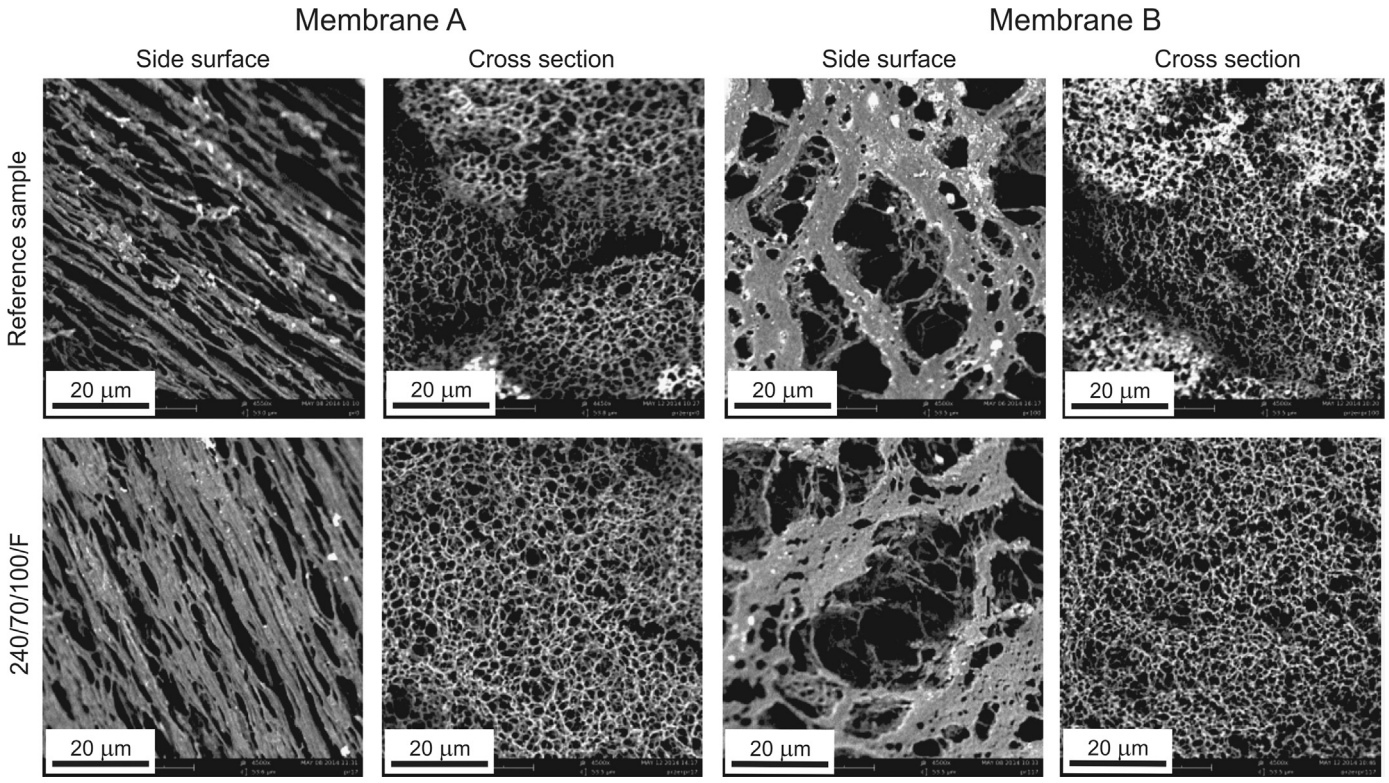

Fig. 1. SEM microphotographs of membranes before and after treatment (Reference samples and samples treated at 240 bar, 70 °C, for 100 min and with fast decompression).

with the maximum and minimum values obtained after $scCO_2$ treatment, including the relative change in % and the treatment conditions, at which those extreme values were obtained.

Scanning electron microscopy allows investigating morphological properties of solid materials and is a popular tool in membrane science and technology [14]. In Fig. 1, SEM microphotographs of reference samples and exemplary samples, treated with $scCO_2$ at the most severe conditions (24 MPa, 70 °C, 100 min, and fast decompression), are depicted. One can notice that the morphologies of Membrane A and B are different: the pores of Membrane A are slightly smaller and they exhibit a denser arrangement, and the side surface of this membrane is characterized by longitudinal fibers, while the side surface of Membrane B has large oval pores. On the other hand, neither destruction nor unfavorable changes in sample structures could be identified in the SEM micrographs for any of the treated samples – the initial morphology was preserved.

During operation, microfiltration membranes are exposed to mechanical stresses resulting from fluid flow and trans-membrane pressure, which usually reaches up to 1 bar. The membrane should withstand these conditions without changing its shape, as it would affect the microfiltration process. Tensile tests enable to assess the basic mechanical properties of the membranes. The experimental results are summarized in Table 1. The Young's modulus, which describes the stiffness of the membrane, did not change noticeably in any of the treated samples. The same applies to ultimate tensile strength, which is a measure of mechanical strength of the material. For one specific test case with Membrane A as test material, the $scCO_2$ treatment caused a drastic decrease of the value of elongation at break, which is – however – not a disqualifying result, as long as the ultimate tensile strength is high enough. In general, the results obtained for Membrane A were characterized by a larger standard deviation than in the case of Membrane B, which suggest the existence of a higher degree of non-uniformity. However, based on the tensile tests, no critical degradation of the mechanical properties of the membrane could be identified.

The wetting properties of microfiltration membranes are an important feature describing their surface quality. Low values of contact angle indicate good wettability of the membrane, which is beneficial during the start-up phase of microfiltration processes. On the other hand, in processes such as membrane distillation, hydrophobic character of the membrane enhances the process performance. Polypropylene membranes are regarded as hydrophobic. Contact with $scCO_2$ should not induce considerable changes of wetting characteristic, so that the treated membrane preserves required properties for a specific application, for which it was designed. Therefore, the advancing and receding contact angle values were measured. The results are presented in Fig. 2, while the reference, minimum and maximum values are also listed in Table 1. Membrane B has higher values of the advancing contact angle than Membrane A; for the receding contact angle, the opposite applies. The measured values remained nearly constant after treatment with $scCO_2$ and no clear trend of changes could be observed. However, this can be also caused by non-uniformity of the initial properties of the membrane samples. As in the tensile test, no membrane degradation could be noted.

Another important characteristic of microfiltration membranes is the pore size distribution, which directly affects the filtration performance. The pore size distribution, as well as the filtration coefficient UFC describing the permeability of the membrane, were investigated using the bubble point experiments. The results are summarized in Table 1. Membrane A has lower values of mean pore size and pore size SD and higher values of the number of pores than Membrane B. On the other hand, Membrane B has higher permeability due to larger pores and higher porosity. As in the previous analytical methods, no negative impact of $scCO_2$ treatment could be observed. Especially, no increase of pore sizes was detected, which would negatively influence the filtration properties of the membranes. For some cases, the increase of pore

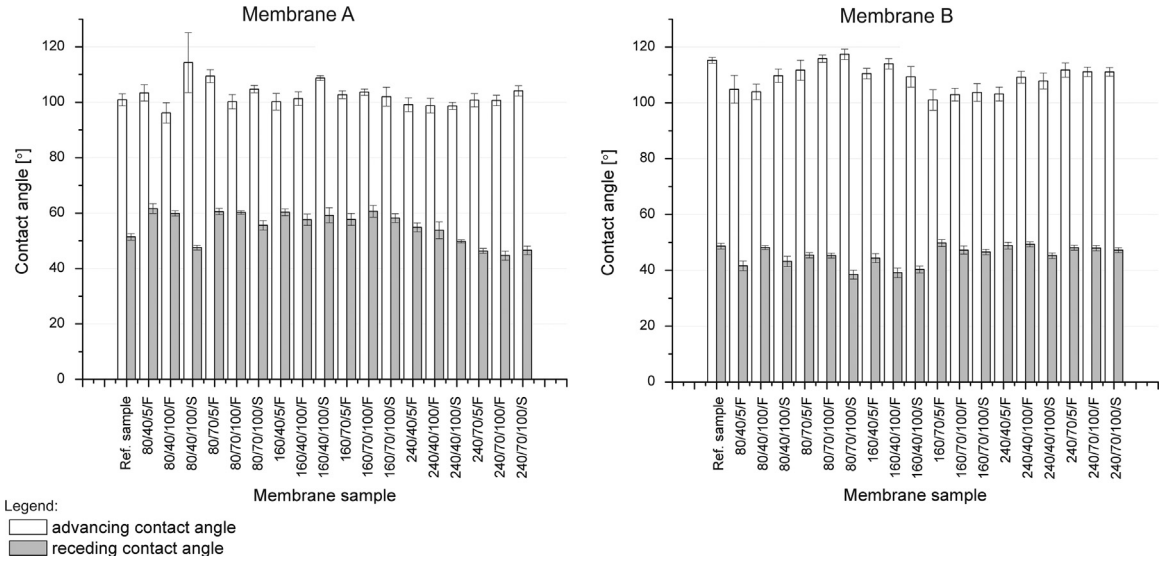

Fig. 2. Results of contact angle measurement (process conditions: pressure [MPa]/temperature [°C]/time [min]/decompression mode (S–slow or F–fast).

number or permeability (UFC) was observed, which is a positive effect, as it enhances the microfiltration performance.

To sum up, no critical changes, which would limit the usability of the treated membranes in microfiltration processes, were identified in the investigated range of process parameters. Bigger differences in the morphology and properties of the two types of investigated membranes (Membranes A and B) are present, than for a given type of membrane before and after $scCO_2$ treatment at various process conditions. The variability of the measured quantities is mainly caused by non-uniformity of the membrane structure and not by treatment with $scCO_2$ at different process conditions. In the bubble point tests, an increase of permeability of the membranes was detected, which can be beneficial for the microfiltration process. No clear influence of varying process pressure, temperature, time and decompression rate on the outcome of the experiments could be determined. Hence, supercritical carbon dioxide can be applied in polypropylene membrane processing technologies without affecting the membrane's properties.

4. Conclusions

Changes of structure and properties of two types of commercial porous polypropylene microfiltration membranes by treatment with $scCO_2$ were investigated. The SEM analysis proved visible differences in the microstructure of both types of membranes, but no noticeable changes of the porous structure after treatment with $scCO_2$. The tensile tests and contact angle measurements also revealed differences of properties between the two membrane types, but no critical changes induced by $scCO_2$. The bubble point tests revealed a slight increase of the number of pores and permeability after $scCO_2$ treatment for some of the test samples, which can be beneficial in terms of microfiltration performance. Hence, no critical changes in membrane structure and properties, which would limit the usability of the membranes in microfiltration processes, were observed. In the investigated process parameter range, supercritical carbon dioxide can be applied as a promising green solvent in polypropylene membrane production, maintenance and modification processes.

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